

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SUPPLEMENTAL ON-LINE MATERIAL, INFLUENCE OF pH ON PLUTONIUM DESORPTION/SOLUBILIZATION FROM SEDIMENT

by

DANIEL KAPLAN

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

Additional Authors:

DOE Contract No. **DE-AC09-96SR18500**

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

Supplemental On-Line Material

Influence of pH on Plutonium Desorption/Solubilization from Sediment

Daniel I. Kaplan,* † Brian A. Powell, § Leo Gumapas, † John T. Coates, † and Robert A. Fjeld †

† Savannah River National Laboratory, Aiken, South Carolina, 29808

‡ Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California

§ Department of Environmental Engineering & Science, Clemson University, Clemson, South Carolina, 29634

* Corresponding author's phone: (803) 725-2363; fax: (803) 725-4704; e-mail: daniel.kaplan@srnl.doe.gov

Oxidation State Analysis Technique. The oxidation state distribution of Pu in each sample for each reaction time was measured using a combined ultrafiltration and solvent extraction technique (I-4). First the oxidation state distribution of aqueous Pu is measured. Then the total system (solid and aqueous phase combined) Pu oxidation state distribution is measured by lowering the pH to leach Pu from the solid phase.

For each reaction time, a 2.5-mL aliquot of the aqueous phase was removed and passed through a 12-nm filter (Microsep 30K MWCO Centrifugal Device; Pall Corporation, East Hills, NY). An aliquot of the filtrate was removed to determine the aqueous phase Pu concentration, and oxidation state distribution in the remaining filtrate was measured using the parallel solvent extraction technique discussed above. These data can be used to express the concentration and oxidation state distribution of Pu in the aqueous phase (Equation 1).

$$[Pu]_{aq} = [Pu(IV)]_{aq} + [Pu(V)]_{aq} + [Pu(VI)]_{aq} \quad (1)$$

The pH of the remaining sample, aqueous and solid phase, was lowered to 1.5 using HClO₄ and mixed for 15 minutes to quantitatively leach Pu(V) and Pu(VI) from the mineral surface. Quantitative leaching of Pu(V) and Pu(VI) was verified using Np(V) and U(VI) as oxidation state analogs. Incomplete leaching of tetravalent actinides was quantified and accounted for in the determination of the Pu oxidation state distribution by assuming that any Pu remaining on the solid phase was Pu(IV). The Pu mass balance for the total system (solid and aqueous phases) is expressed in Equation 2:

$$m_{Total}^{Pu} = [Pu(IV)]_{aq} V_{aq} + [Pu(IV)]_{solid} m_{solid} + [Pu(V)]_{aq} V_{aq} + [Pu(V)]_{solid} m_{solid} + [Pu(VI)]_{aq} V_{aq} + [Pu(VI)]_{solid} m_{solid} \quad (2)$$

where m is the mass of the solid phase (g), V is the volume of the aqueous phase (L), and $[Pu(IV)]$, $[Pu(V)]$, and $[Pu(VI)]$ are the concentrations of Pu in these oxidation states (mol/L)

45 or mol/g). Again, the $[Pu(X)]_{aq}$ parameters were measured in the aqueous phase in contact with
46 the solid phase and $[Pu(X)]_{solid}$ parameters were measured in the filtered pH 1.5 extracts. The Pu
47 distribution among the three oxidation states is expressed as a fraction to account for both the
48 solid phase and aqueous phase contributions (Equation 3).

49

$$50 \quad f_{aq+solid}^{Pu(Total)} = 1.0 = f_{aq+solid}^{Pu(IV)} + f_{aq+solid}^{Pu(V)} + f_{aq+solid}^{Pu(VI)} \quad (3)$$

51

52 As an experimental control, single oxidation state Pu(IV), Pu(V), and Pu(VI) solutions remained
53 as $98 \pm 4\%$ Pu(IV), $97 \pm 4\%$ Pu(V), and $98 \pm 2\%$ Pu(VI) after being carried through the ultra-
54 filtration/ solvent extraction oxidation state analysis technique described above. The integrity of
55 the initial oxidation state was maintained throughout the procedure, validating the stability of
56 each oxidation state as well as the separation method in 0.01 M NaCl.

57

58 **Validation of Oxidation State Analysis Procedure.** Aliquots of $^{230}\text{Th(IV)}$, $^{237}\text{Np(V)}$, or
59 $^{233}\text{U(VI)}$ were mixed with hausmannite and pyrolusite suspensions at pH 8 for one hour. Then
60 the solutions were acidified and the actinides were leached for various times and passed through
61 12-nm filters. The concentration of the oxidation state analogues in the leachate was measured
62 using liquid scintillation counting. It was found that a 15 minute leaching step was sufficient to
63 obtain quantitative leaching of Np(V) and U(VI) from the solid phase. Quantitative leaching of
64 Th(IV) was not achieved in 15 minutes. Therefore any Pu remaining on the solid phase following
65 a 15 minute leaching step was assumed as Pu(IV).

66

67
68
69
70**Plutonium Sorption as a Function of pH:**

Table S1. Apparent Solubility (mol L⁻¹) and Apparent Distribution Coefficients (K_d; mL/g) of Pu as a Function of pH.								
pH	Pu(IV)–1 day		Pu(V)–1 day		Pu(V)–33 days		Desorption–24 yr	
	Solubility	K _d	Solubility	K _d	Solubility	K _d	Solubility	K _d
4	9.5e-8	25	1.3e-7	5	4.3e-10	58,000	2.3e-8	1570
5	7.5e-8	38	7.5e-8	24	3.3e-10	80,000	3.6e-9	10,200
6	3.2e-9	1330	9.2e-9	341	8.3e-11	342,000	7.5e-10	49,500
7	1.1e-9	3930	7.5e-10	4430	4.2e-11	687,000	1.2e-10	346,000
8	6.6e-10	6400	5.6e-10	5740	NA	NA	2.3e-11	1,639,000

71

72

Literature Cited

73

74

75

76

77

78

79

80

81

82

83

84

85

86

87

1. Keeney-Kennicutt, W. L.; Morse, J. W. The redox chemistry of Pu(V)O₂⁺ interactions with common mineral surfaces in dilute solutions and seawater. *Geochim. Cosmochim.* **1985**, *49*, 2577–2588.
2. Neu M. P.; Hoffman D. C.; Roberts K. E.; Nitsche H.; Silva R. J. Comparison of chemical extractions and laser photoacoustic spectroscopy for the determination of plutonium species in near-neutral carbonate solutions. *Radiochimica Acta* **1994**, *66*, 265–272.
3. Powell, B. A.; Fjeld, R. A.; Kaplan, D. I.; Coates, J. T.; Serkiz, S. M. Pu(V)O₂⁺ adsorption and reduction by synthetic magnetite (Fe₃O₄). *Environ. Sci. Technol.* **2004**, *38*, 6016–6024.
4. Morgenstern, A.; Choppin, G. R. Kinetics of the oxidation of Pu(IV) by manganese oxide. *Radiochim. Acta* **2002**, *90*, 69–74.